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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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AS

In re the application of:

MINORU WAKI

Group Art Unit: 1714

Serial Number: 09/673,194

Examiner: Shosho, Callie E.

Filed: October 12, 2000

For: WATER-BASED PIGMENT DISPERSION, PROCESS FOR  
PREPARING THE SAME AND WATER-BASED INK CONTAINING THE  
SAME

DECLARATION UNDER 37 CFR 1.132

Honorable Commissioner

Washington, D.C. 20231

RECEIVED  
MAY 27 2003  
GROUP 1700

Sir,

I, Minoru Waki, the inventor residing at c/o MIKUNI SHIKISO  
KABUSHIKI KAISHA, 101, Kokubunji, Mikunino-cho, Himeji-shi,  
HYOGO, JAPAN duly deposes and says:

1. That I graduated from Himeji Institute of Technology,  
Japan in the year 1978;

2. That I have been employed in MIKUNI SHIKISO  
KABUSHIKI KAISHA since 1978;

3. That I have been engaged in research and development;

4. That I have read and am familiar with the instant  
application for United States Letters Patent and Office Action thereto  
mailed February 21, 2003; and

5. That I have made experiments in order to prove the fact  
that a water-based pigment dispersion of the present invention in

which a thermoplastic resin containing the carboxylic group is cross-linked with a cross-linking agent is more excellent than a dispersion in which a cross-linking agent is merely contained and a thermoplastic resin containing the carboxylic group is not cross-linked with a cross-linking agent.

### EXPERIMENTS

The following experiments prove that a water-based pigment dispersion of the present invention in which a thermoplastic resin containing a carboxylic group is cross-linked with a cross-linking agent is more excellent in property such as storage stability during the passage of time than a dispersion in which a cross-linking agent is contained but a thermoplastic resin containing a carboxylic group is not cross-linked with a cross-linking agent.

#### EXPERIMENT 1

##### [Predispersion Step]

The following components were prepared and predispersed by kneading in a kneader at room temperature for 1 hour to give a mixture. Hereinafte, "part(s) by weight" is referred to as "part(s)" hereinafter.

Component	Amount (part(s))
Yellow pigment (Pigment yellow 14 (C.I.21095))	65
Styrene-acrylic acid copolymer (styrene/acrylic acid (weight ratio) = 88/12, acid value: 94, number average molecular weight: 12000)	30
Ethylene glycol	5

Then, 5 parts of 25% ammonia water and 370 parts of ion-exchange water were added to the mixture. These were stirred at 80°C for 3 hours, so that the styrene-acrylic acid copolymer was neutralized and dissolved (neutralization rate: about 150 %).

[Dispersion Step]

The thus predispersed and neutralized mixture was subjected to three-pass treatment in a sand mill which was filled with glass beads having a diameter of 0.7 mm in a volume of 80 %. As a result, the yellow pigment was finely dispersed with the styrene-acrylic acid copolymer to give a dispersion.

Then, part of ammonia in the above dispersion was removed by an evaporator and pH of the dispersion was adjusted to 7.0.

[Cross-linking treatment Step]

To the above dispersion having pH of 7.0 was added 5 parts of 30 % aqueous carbodiimide resin (carbodiimide equivalent: 300), and these were stirred at 90°C for 5 hours. As a result, the styrene-acrylic acid copolymer in the dispersion was cross-linked (gel percent of cross-linked styrene-acrylic acid copolymer: 40 %, number average molecular weight of cross-linked styrene-acrylic acid copolymer:

500000). Then, the cross-linked styrene-acrylic acid copolymer was strongly adsorbed on the yellow pigment. The pH of the dispersion at finishing cross-linking reaction was 6.8.

[Adjust Step of pH]

To the dispersion containing the yellow pigment and the cross-linked styrene-acrylic acid copolymer strongly adsorbed thereon was added triethanolamine in an amount of 0.3 % by weight, so that pH of the dispersion was adjusted to 8.7.

The dispersion was subjected to centrifugal separation at 25000 G for 5 minutes, and coarse large particles were removed. As a result, a yellow water-based pigment dispersion having solid matter concentration of 20 % by weight was prepared.

The average particle size of pigment in the yellow water-based pigment dispersion was 130 nm and absorbancy ratio was 30.

As to the water-based pigment dispersion, light resistance and stability during the passage of time were examined in accordance with the following methods. The results are shown in TABLE 1.

(i) Light resistance Test

The water-based pigment dispersion was coated on Kent paper by a barcoater No. 10, and the Kent paper was dried at 120 °C for 10 minutes to give a test piece.

The test piece was irradiated with ultraviolet ray for 300 hours by using a carbon arc-fade meter, and color difference ( $\Delta E$ ) was measured by using CCM (ACS-2018 Model 55SX, made by ACS Company). Then, degree of color tone change was examined.

When the light resistance is more excellent, the color difference becomes smaller. When the color difference is less than 3.0, the light resistance is excellent.

(ii) Stability during the passage of time

After the water-based pigment dispersion was allowed to stand in a thermostated room at 20 °C for 1 month, existence of separation of the pigment, water-floating and precipitation was examined. When there is even a little separation of the pigment, a little water-floating or a little precipitation, the evaluation is unusual.

In TABLE 1, when the evaluation is not unusual, the mark is "O". When the evaluation is unusual, the mark is "X".

COMPARATIVE EXPERIMENT 1

A yellow water-based pigment dispersion was obtained by the same manner as in EXPERIMENT 1 except that 30 % aqueous carbodiimide resin was added and stirred but not heated in cross-linking treatment step so that cross-linking reaction was not occurred.

EXPERIMENT 2

[Predispersion Step]

The following components were prepared and predispersed by kneading in a kneader at room temperature for 1 hour to give a mixture.

<u>Component</u>	<u>Amount (Part(s))</u>
Red pigment (Pigment red 22 (C.I.12315))	70
Styrene- $\alpha$ -methylstyrene-acrylic acid copolymer (styrene/ $\alpha$ -methylstyrene/acrylic acid (weight ratio) = 40/30/30, acid value: 234, number average molecular weight: 9000)	28
<u>Glycerin</u>	<u>2</u>

Then, 12 parts of triethylamine and 345 parts of ion-exchange water were added to the mixture. These were stirred at 70°C for 3 hours, so that the styrene- $\alpha$ -methylstyrene-acrylic acid copolymer was neutralized and dissolved (neutralization rate: about 100 %).

[Dispersion Step]

The thus predispersed and neutralized mixture was subjected to three-pass treatment in a sand mill which was filled with zirconia beads having a diameter of 0.5 mm in a volume of 80 %. As a result, the red pigment was finely dispersed with the styrene- $\alpha$ -methylstyrene-acrylic acid copolymer to give a dispersion.

Then, 1.5 parts of polyoxyethylene alkylphosphate was added to the above dispersion and pH of the dispersion was adjusted to 6.5.

[Cross-linking treatment Step]

To the above dispersion having pH of 6.5 was added 5 parts of 30 % aqueous carbodiimide resin (carbodiimide equivalent: 300), and these were stirred at 80°C for 7 hours. As a result, the styrene- $\alpha$ -methylstyrene-acrylic acid copolymer in the dispersion was cross-linked (gel percent of cross-linked styrene- $\alpha$ -methylstyrene-acrylic

acid copolymer: 70 %, number average molecular weight of cross-linked styrene- $\alpha$ -methylstyrene-acrylic acid copolymer: 800000). Then, the cross-linked styrene- $\alpha$ -methylstyrene-acrylic acid copolymer was strongly adsorbed on the red pigment. The pH of the dispersion at finishing cross-linking reaction was 6.4.

[Adjust Step of pH]

To the dispersion containing the red pigment and the cross-linked styrene- $\alpha$ -methylstyrene-acrylic acid copolymer strongly adsorbed thereon was added ammonia water in an amount of 0.5 % by weight, so that pH of the dispersion was adjusted to 9.2.

The dispersion was subjected to centrifugal separation at 25000 G for 5 minutes, and coarse large particles were removed. As a result, a red water-based pigment dispersion having solid matter concentration of 20 % by weight was prepared.

The average particle size of pigment in the red water-based pigment dispersion was 163 nm and absorbancy ratio was 55.

As to the water-based pigment dispersion, light resistance and stability during the passage of time were examined in the same manner as in EXPERIMENT 1. The results are shown in TABLE 1.

### COMPARATIVE EXPERIMENT 2

A red water-based pigment dispersion was obtained by the same manner as in EXPERIMENT 2 except that 30 % aqueous carbodiimide resin was added and stirred but not heated in cross-linking treatment step so that cross-linking reaction was not occurred.

### EXPERIMENT 3

[Predispersion Step]

The following components were prepared and predispersed by kneading in a butterfly mixer at room temperature for 5 hour to give a mixture.



<u>Component</u>	<u>Amount (part(s))</u>
Blue pigment (Pigment blue 15:1 (C.I.74160))	40.0
Styrene-maleic acid copolymer (styrene/maleic acid (weight ratio) = 60/40, acid value: 190, number average molecular weight: 3000)	7.0
Ethylene glycol	5.0
Diethylamine	2.5
<u>Ion-exchange water</u>	<u>45.5</u>

Then, 150 parts of ion-exchange water was added to the mixture. These were stirred for 30 minutes, so that the styrene-maleic acid copolymer was neutralized and dissolved (neutralization rate: about 120 %).

[Dispersion Step]

The thus predispersed and neutralized mixture was subjected to five-pass treatment in a sand mill which was filled with glass beads having a diameter of 1.0 mm in a volume of 80 %. As a result, the blue pigment was finely dispersed with the styrene-maleic acid copolymer to give a dispersion.

Then, one part of morpholine in the above dispersion was removed by evaporator and pH of the dispersion was adjusted to 7.2.

[Cross-linking treatment Step]

To the above dispersion having pH of 7.2 was added 5 parts of 35 % aqueous oxazoline group-containing resin (oxazoline equivalent: 200), and these were stirred at 90°C for 3.5 hours. As a result, the styrene-maleic acid copolymer in the dispersion was

cross-linked (gel percent of cross-linked styrene-maleic acid copolymer: 50 %, number average molecular weight of cross-linked styrene-maleic acid copolymer: 550000). Then, the cross-linked styrene-maleic acid copolymer was strongly adsorbed on the blue pigment. The pH of the dispersion at finishing cross-linking reaction was 7.0.

[Adjust Step of pH]

To the dispersion containing the blue pigment and the cross-linked styrene-maleic acid copolymer strongly adsorbed thereon was added N-methyl-diethanolamine in an amount of 0.3 % by weight, so that pH of the dispersion was adjusted to 9.5.

The dispersion was subjected to centrifugal separation at 25000 G for 5 minutes and coarse large particles were removed. As a result, a blue water-based pigment dispersion having solid matter concentration of 20 % by weight was prepared.

The average particle size of pigment in the blue water-based pigment dispersion was 138 nm and absorbancy ratio was 43.

As to the water-based pigment dispersion, light resistance and stability during the passage of time were examined in the same manner as in EXPERIMENT 1. The results are shown in TABLE 1.

### COMPARATIVE EXPERIMENT 3

A blue water-based pigment dispersion was obtained by the same manner as in EXPERIMENT 3 except that 35 % aqueous oxazoline group-containing resin was added and stirred but not heated in cross-linking treatment step so that cross-linking reaction was not occurred.

#### EXPERIMENT 4

##### [Predispersion Step]

The following components were prepared and predispersed by kneading in a butterfly mixer at room temperature for 4 hours to give a mixture.

<u>Component</u>	<u>Amount (Part(s))</u>
Green pigment (Pigment green 7 (C.I.74260))	35.0
Styrene-methacrylic acid copolymer (styrene/mathacrylic acid (weight ratio) = 78/22, acid value: 170, number average molecular weight: 85000)	8.5
Diethylene glycol	10.0
Isopropylamine	2.0
<u>Ion-exchange water</u>	<u>43.5</u>

Then, 110 parts of ion-exchange water was added to the mixture. These were stirred for 30 minutes, so that the styrene-mathacrylic acid copolymer was neutralized and dissolved (neutralization rate: about 130 %).

##### [Dispersion Step]

The thus predispersed and neutralized mixture was subjected to three-pass treatment in a sand mill which was filled with zirconia beads having a diameter of 0.5 mm in a volume of 80 %. As a result, the green pigment was finely dispersed with the styrene-methacrylic acid copolymer to give a dispersion (pH: 8.2).

[Cross-linking treatment Step]

To the above dispersion having pH of 8.2 was added 5 parts of 100 % aqueous polyoxyethylene oligoester acrylate (difunctionality in a molecule), and these were stirred at 85°C for 8 hours. As a result, the styrene-methacrylic acid copolymer in the dispersion was cross-linked (gel percent of cross-linked styrene-methacrylic acid copolymer: 60 %, number average molecular weight of cross-linked styrene-methacrylic acid copolymer: 700000). Then, the cross-linked styrene-methacrylic acid copolymer was strongly adsorbed on the green pigment. The pH of the dispersion at finishing cross-linking reaction was 7.5.

[Adjust Step of pH]

To the dispersion containing the green pigment and the cross-linked styrene-methacrylic acid copolymer strongly adsorbed thereon was added triethanolamine in an amount of 0.3 % by weight, so that pH of the dispersion was adjusted to 9.1.

The dispersion was subjected to centrifugal separation at 25000 G for 5 minutes and coarse large particles were removed. As a result, a green water-based pigment dispersion having solid matter concentration of 20 % by weight was prepared.

The average particle size of pigment in the green water-based pigment dispersion was 117 nm and absorbancy ratio was 37.

As to the water-based pigment dispersion, light resistance and stability during the passage of time were examined in the same manner as in EXPERIMENT 1. The results are shown in TABLE 1.

COMPARATIVE EXPERIMENT 4

A green water-based pigment dispersion was obtained by the same manner as in EXPERIMENT 4 except that 100 % aqueous polyoxyethylene oligoester acrylate was added and stirred but not heated in cross-linking treatment step so that cross-linking reaction was not occurred.

TABLE 1

EXPERIMENT No.	Property of water-based pigment dispersion	
	Light resistance (Color differences ( $\Delta E$ ))	Stability during the passage of time
1	1.9	O
COM. EX. 1	2.1	X
2	2.2	O
COM. EX. 2	2.3	X
3	0.5	O
COM. EX. 3	0.6	X
4	0.3	O
COM. EX. 4	0.3	X

From the results shown in TABLE 1, it can be understood that water-based pigment dispersions prepared in EXPERIMENTS 1 to 4 accordance with the process of the present invention show excellent light resistance and excellent stability during the passage of time.

To the contrary, it can be understood that water-based pigment dispersions prepared in COMPARATIVE EXPERIMENTS 1 to 4 without heating step for cross-linking show bad stability during the passage of time in addition to same or worse light resistance in comparison with

those of EXPERIMENTS 1 to 4 with heating step for cross-linking respectively.

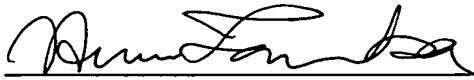
The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

This 8th day of May, 2003

Minoru Waki

Minoru Waki

We, the undersigned witnesses, hereby acknowledge that Minoru Waki personally known to us and did execute the foregoing Declaration in our presence on:

Date: May 10, 2003      Witness 

Date: MAY 9, 2003      Witness 